Heteroatom Chemistry
Volume 4, Number 4, 1993

Crystal and Molecular Structure and the Absolute Configuration of N-Phenyl-N′-(1-Phenylethyl)methanephosphonodiamidate

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Received 1 June 1992

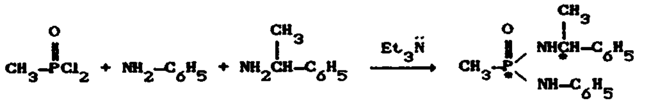
ABSTRACT

The structural investigation of the product of the reaction of methanephosphonodichloridate with R(+)-1-phenylethylamine and aniline in the presence of triethylamine [3] was performed. The obtained compound $C_{15}H_{19}N_2OP$ *(1) crystallizes in monoclinic system, space group* $P2_1$ *with* $a = 10.466(1)$ Å, $b = 6.984(3)$ Å, $c = 10.471(2)$ Å, $\beta = 95.43(1)°$, $V = 762.0(9)$ Å^3. $Z = 2$, *and* $R = 0.037$. *The absolute configuration at the P and C8 atoms was determined by means of X-ray crystallography as* R_p *and* R_{C8}, *respectively.*

INTRODUCTION

The reaction of N-metallated phosphoramidates, derivatives of primary amines, with such electrophiles as carbon dioxide, carbon disulfide, and carbon diselenide, leading to phosphates, phosphorothioates, and phosphoroselenoates, respectively [1], quoted sometimes as Stec's reaction [2], opened a new route to numerous P-chiral organophosphates [3].

Since the process of PN-PX conversion (X = ^{18}O, S, Se) is fully stereospecific and occurs with the retention of the configuration at phosphorus, the unambiguous assignment of the absolute configuration at phosphorus in the starting phosphoramidate is a crucial precondition for the broad application of the aforementioned phosphoramidates. With that in mind, we undertook studies of the configurational assignment at phosphorus in diastereoisomers of N-phenyl-N′-(1-phenylethyl)-methanephosphonodiamidate (**1**) (Scheme 1). The compounds were obtained according to the methodology described earlier [3], and the crystals of the separated diastereoisomer of mp 161–163°C, δ_{31P} 23.2 ($CDCl_3$), $[\alpha]_D^{20} = +53.1°$ (c 1.5; MeOH) appeared to be suitable for X-ray analysis.



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SCHEME 1

RESULTS AND DISCUSSION

The general view of the molecule of **1** is shown in Figure 1. The molecule of compound **1** has two chiral centers at the P and C8 atoms. The absolute configuration was established by the Hamilton test, and, independently, by calculating the ETA value

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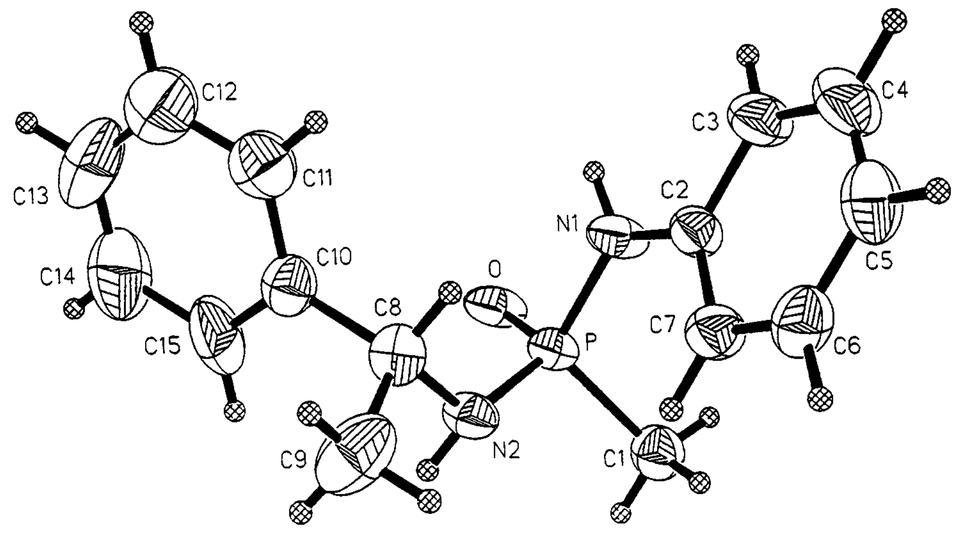
FIGURE 1 ORTEP view of the molecule of **1** with atom numbering.



[4,5]. The model of the structure was refined with the reversed signs of all f″ values. The resulting R$^-$-factor is 0.03748 (R$^+$ was calculated as 0.03752). The lower value of the R$^-$-factor for the reversed model indicates greater probability of the reversed configuration; therefore, the finally established absolute configuration is R_p and R_{c8}. The calculated value of the $\mathfrak{R}$-ratio equals 1.0011, from which $\alpha \leq 1 \cdot 10^{-2}$ [6]. Table 1 contains the coordinates of nonhydrogen atoms and of the hydrogen atoms bonded to nitrogen. The negative values of coordinates are left to show the reversal of them for the R$^-$ calculation. Table 2 contains the selected bond lengths and valence angles. Hydrogen atoms bonded to carbon atoms are placed geometrically with a C—H distance of 0.95 Å and are not specified in the tables.

The difference between the P–N1 and P–N2 bond lengths (see Table 2) equals 10σ and occurs in the majority of compounds of that type (i.e., those containing N–P–N and P=O bonds) found in the literature [7]. This difference is between 0.003 Å and 0.023 Å, depending on the bonds around the nitrogen and phosphorus atoms (if these bonds are in the ring, then the difference is larger due to ring strain) and the accuracy of the measurement. The average P–N1 and P–N2 bond lengths calculated from 25 structures found in the literature [7] are equal to 1.650(4) Å and 1.653(4) Å, respectively.

Two phenyl rings at the edge of the molecule are bent towards each other at the angle of 47.2(1)° and the planes N1–P–O and N2–P–O are at the angle 60.3(2)°. The sum of the valence angles (359.9(4)° and 346.2(4)°, respectively) is a proof of the different geometry of the P–N1 and P–N2 bonds as well as of the different arrangement of the free electron pairs at the N1 and N2 atoms; these can be seen from Newman projections (Figures 2 and 3).

TABLE 1 Positional Parameters for the Selected Atoms with Esd's in Parentheses

	x	*y*	*z*
P	−0.91101(7)	−0.136	−0.91497(6)
O	−0.9975(2)	−0.0982(3)	−1.0330(2)
N1	−0.8698(3)	0.0713(4)	−0.8457(2)
N2	−0.9676(2)	−0.2669(4)	−0.8029(2)
C1	−0.7698(3)	−0.2598(5)	−0.9530(3)
C2	−0.7858(3)	0.1083(4)	−0.7360(3)
C3	−0.7519(3)	0.2996(5)	−0.7099(3)
C4	−0.6726(3)	0.3453(6)	−0.6005(3)
C5	−0.6256(3)	0.2063(6)	−0.5158(3)
C6	−0.6578(3)	0.0167(6)	−0.5430(3)
C7	−0.7376(3)	−0.0328(5)	−0.6514(3)
C8	−1.0455(3)	−0.1957(5)	−0.7052(3)
C9	−1.0454(4)	−0.3443(7)	−0.5994(3)
C10	−1.1813(3)	−0.1388(7)	−0.7535(2)
C11	−1.2330(4)	0.0333(6)	−0.7134(3)
C12	−1.3600(4)	0.0816(7)	−0.7512(4)
C13	−1.4355(4)	−0.0345(8)	−0.8289(4)
C14	−1.3853(4)	−0.2001(9)	−0.8707(5)
C15	−1.2584(4)	−0.2526(7)	−0.8340(4)
HN1[a]	−0.916(1)	0.165(1)	−0.889(1)
HN2[a]	−1.000(1)	−0.374(1)	−0.833(1)

[a]These atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3) \cdot [a^2 \cdot B(1,1) + b^2 \cdot B(2,2) + c^2 \cdot B(3,3) + ab(\cos\gamma) \cdot B(1,2) + ac(\cos\beta) \cdot B(1,3) + bc(\cos\alpha) \cdot B(2,3)]$.

EXPERIMENTAL

A crystal suitable for X-ray diffraction measurement was obtained by crystallization from acetone. Compound **1** crystallizes in the monoclinic system, space group $P2_1$ with the following unit-cell parameters: $a = 10.466(1)$ Å, $b = 6.984(3)$ Å, $c = 10.471(2)$ Å, $\beta = 95.43(1)°$, $Z = 2$, $D_c = 1.196(2)$

TABLE 2 Selected Bond Distances (Å) and Bond Angles (°) with Esd's in parentheses

P–O	1.485(3)
P–N1	1.660(2)
P–N2	1.641(2)
P–C1	1.789(3)
N1–C2	1.404(4)
N2–C8	1.454(4)
C8–C9	1.518(5)
C8–C10	1.516(5)
N1–HN1	0.91(1)
N2–HN2	0.87(1)
O–P–N1	108.6(1)
O–P–N2	117.5(1)
O–P–C1	110.7(1)
N1–P–N2	105.6(1)
N1–P–C1	109.4(1)
N2–P–C1	104.7(1)
P–N1–C2	129.4(3)
P–N1–HN1	108(1)
C2–N1–HN1	123(1)
P–N2–C8	125.3(2)
N2–C8–C9	108.6(3)
N2–C8–C10	115.2(2)
N2–C8–H81	107(1)
C9–C8–C10	111.0(3)
C9–C8–H81	110(1)
C10–C8–H81	105(1)
P–N2–HN2	112(1)
C8–N2–HN2	109(1)

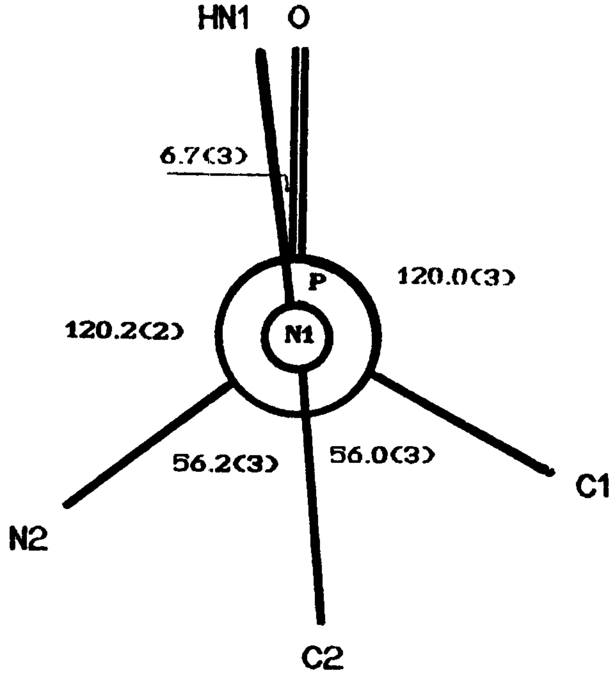


FIGURE 2 Newman projection perpendicular to N1–P bond.

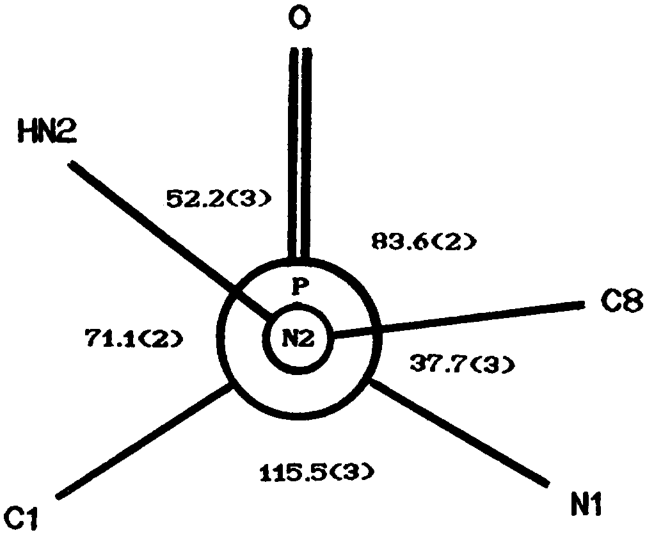


FIGURE 3 Newman projection perpendicular to N2–P bond.

g/cm^3, μ = 1.7 cm^{-1}, V = 762.0(9) Å^3, $\lambda(\mathrm{Mo}K_\alpha)$ = 0.7093 Å.

Intensity data were collected using a CAD4 diffractometer in the θ range $1 \leq \theta \leq 30°$ with graphite monochromatized MoK_α radiation. Lattice constants were refined by the least-squares fit of 25 reflections in the θ range of 9.8–13.9°. A total of 2497 integrated reflections were collected in $\omega/2\theta$ scan technique, scan width $(0.92 \pm 0.35 \tan \theta)°$; range of measurement $0 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 9$, $-14 \leqslant l \leqslant 14$. The decline in intensities of three standard reflections (−2, −3, 4; 5, 1, −3; 4, −1, −3) was 0.7% during 36.0 hours of exposure. An absorption correction was applied by the EAC program [9] with correction factors: min = 0.9720, max = 0.9999, av = 0.9859; min transmission equaled 94.48%, max = 99.98%, and av = 97.19%. A total of 2098 observed reflections (with $I \geqslant 3\sigma(I)$) were used to solve the structure by direct methods (SHELXS program) [10]. The structure was refined by full matrix least-squares using F's (SDP computing) [9]. The H atoms were placed geometrically at idealized positions (except for the HN1 and HN2 atoms which were found from a difference Fourier map) and refined isotropically as riding. Anisotropic thermal parameters were refined for all nonhydrogen atoms. The final refinement converged to R = 0.037 with unit weight for 191 refined parameters. The largest shift/error parameter in the last cycle was 0.02. The final difference Fourier map did not show any peaks higher than 0.329 eÅ^{-3}.

All calculations were carried out with the Enraf-Nonius SDP crystallographic computing package [9] (except for direct methods which were performed with the SHELXS program [10]). Scattering factors were taken from the *International Tables for X-ray Crystallography* [11]. Values of $F_{\mathrm{obs}}/F_{\mathrm{calc}}$ and the other full crystallographic data* of compound 1 are deposited at the Cambridge Crystallographic Data Centre [8].

ACKNOWLEDGMENTS

The authors are grateful to Prof. W. J. Stec for consultations and valuable discussions and to Prof. E. Galas, Director of the Institute of Technical Biochemistry, for his help. This work was financed by the Committee for Scientific Research (KBN) under Grant No. 4 0070 91 01.

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*These tables are standard computer listings, in which standard deviations of data concerned with H-atoms are estimated in the same range as esd's in corresponding C, N atoms, to which these H's are bonded. Correctly, it is necessary to treat esd's in data concerned with H-atoms as one range less than those in the corresponding C, N atoms.